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“Total Mass Accounting in Advanced Liquid-Fueled Reactors”

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Introduction

- How to measure and monitor the mass of molten salt in fuel salt or coolant salt reactor systems?
  - It's hot
  - It's corrosive
  - It's radioactive
  - It's non-accessible
  - Density could change all the time (burn-up, refueling etc)

- Important safeguard requirement for MC&A of advanced reactors

- We propose to add radioactive tracer in which the mass of total volume of salt may be determined - radioactive tracer dilution (RTD) method.

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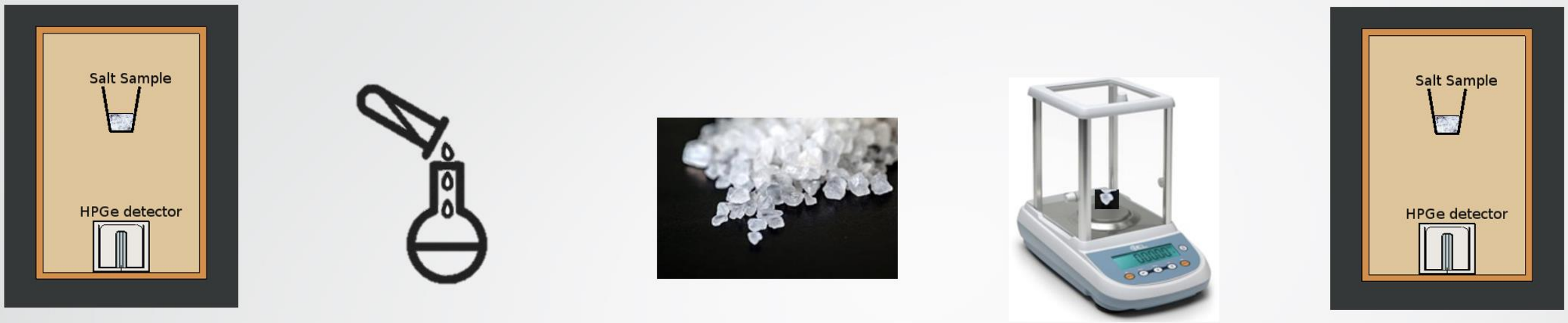
The principle of RTD

Tracer with activity A1 is added to salt of unknown mass, then sampled with known mass and activity of A2.



Measure Activity (A1) → **Spike** → **Sample** → **Weigh (m)** → **Measure Activity (A2)**

Measure Activity (A1)
- Measure activity of Na-22 Salt (tracer)

Spike
- Add Na-22 Tracer to the salt of TBD

Sample
- Sampling

Weigh (m)
- Weigh the mass of the sample

Measure Activity (A2)
- Measure activity of the sample

$$\boxed{Mass_{tot} = \left(\frac{A_1}{A_2}\right) * m_{sample}}$$

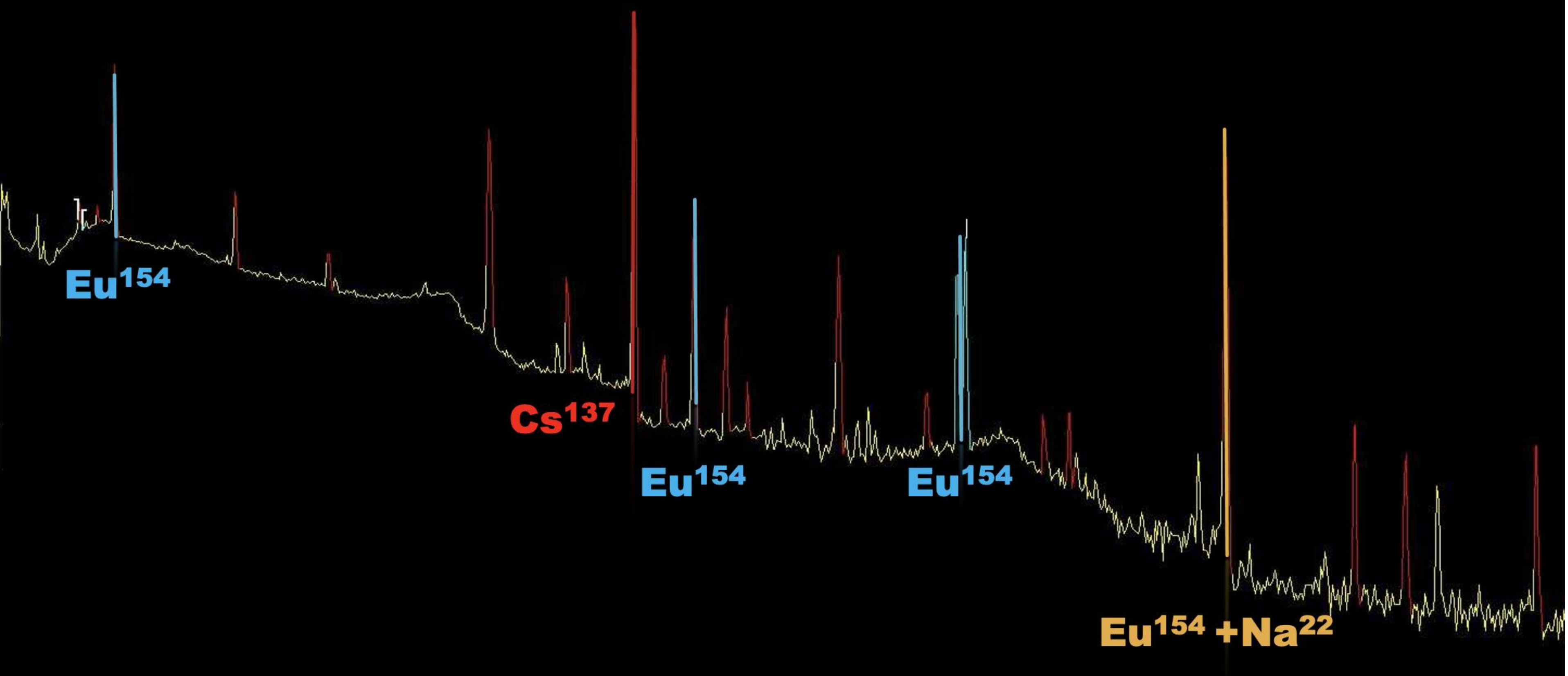
Radioactive tracer selection

^{22}Na has been selected as the proper radioactive tracer.

- It undergoes beta+ decay (non-fission product characteristic)
- known chemical compatibility with actinides and fission products in molten chloride and fluoride salts
- Availability and half life (2.6 y) for handling
- Emits 1274.54 keV gamma-ray (99.94%), high enough to be outside of the Compton plateau of many fission products' gamma-rays in a gamma energy spectrum
- Only known overlapped peak is 1274.43 keV from ^{154}Eu
- High thermal neutron capture cross-section helps to remove Na-22 after spiking

Gamma Spectroscopy of non-fuel salt from previous proof-of-concept study

Gamma Spectrum from 5 g of salt with ^{137}Cs, ^{154}Eu and ^{22}Na



OSU Nuclear Reactor Lab (2018)

Lei Cao et al. "Determination of molten salt mass using Na-22 tracer mixed with Eu-154 and Cs-137." Journal of Radioanalytical and Nuclear Chemistry 318 (2018): 457-463.

Objectives

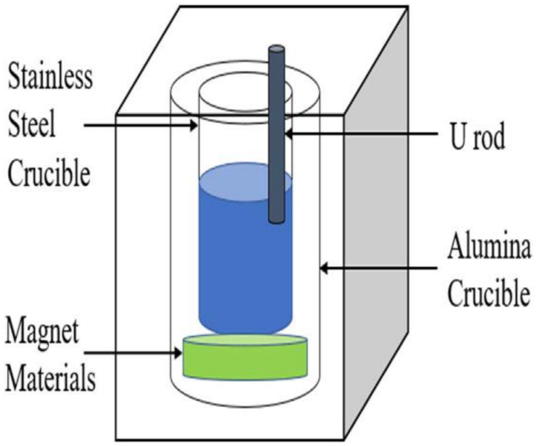
The objective of this research is to validate a radioactive tracer dilution (RTD) method for the irradiated fuel-bearing molten salt mass determination to evaluate the possibilities of its deployment in NMA scenarios, e.g., in molten salt loop in LFMSRs.

Questions to be answered:

Q1.) Are there any other unknown interferences at 1274 keV?
Q2.) Will there be high deadtime caused by other fission products during gamma counting?
Q3.) How to do sampling?
Q4.) How long should IAEA inspector wait before counting?

$MgCl_2$-KCl-UCl_3 salt for irradiation (UoU)

- 13.8 g of $MgCl_2$-KCl-UCl_3 (DU) fuel salt was prepared at the University of Utah
- High purity (99.99%) $MgCl_2$ and KCl was acquired through commercial vendors and mixed with a 0.3:0.7 molar ratio.
- UCl_3 was synthesized by using DU metal rod and $FeCl_2$ in $MgCl_2$-KCl at ~500°C.
- Salt samples were taken and measured by ICP-MS, the U concentration was determined to be 12.16 wt%. The $FeCl_2$ concentration is 0.045 wt%. UCl_3 is 17.6 wt%.
- U-235 concentration in the entire salt is (2.76 mg/13.8 g) = 200 ppm
- $MgCl_2$-KCl-UCl_3 salt will be packed in an argon glovebox and shipped to OSU by a commercial carrier



Schematic for preparing UCl_3 salt from DU metal rod and NaCl-KCl-$FeCl_2$

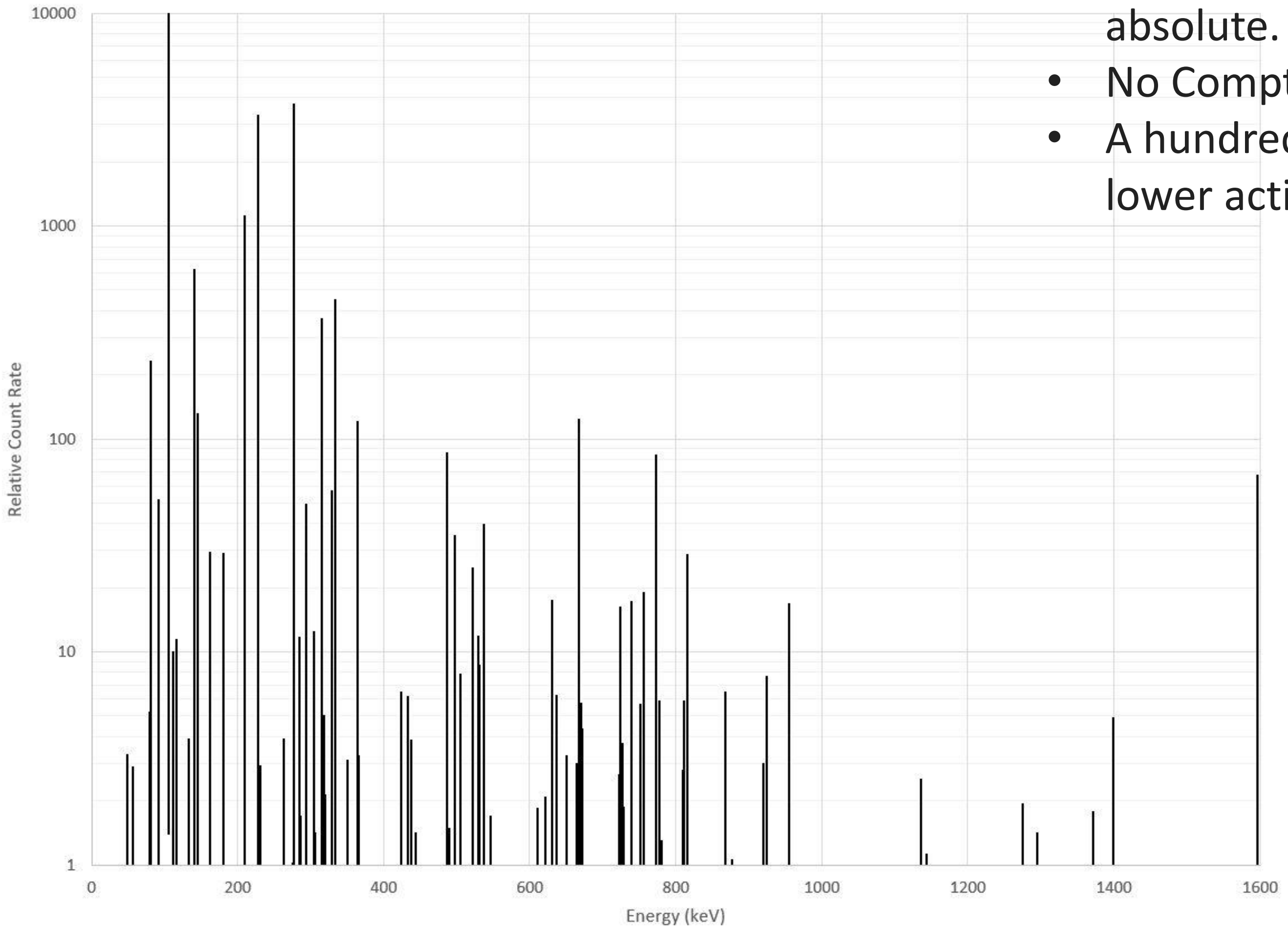
Huan Zhang et al 2021, J. Electrochem. Soc. 168 056521

Gamma spectrum simulation by ORIGEN burnup

- ORIGEN to predict the radionuclide inventory after the irradiation.
- Took all nuclides with activity greater than 10 μCi (a couple dozen).
- For each of those, listed all decay gammas with intensity greater than 1% (~120 gammas).
- Combining the nuclide activity and gamma intensity gives the gamma emission rate
- Then used a representative efficiency curve for the HPGe detector to predict the relative peak count rate for each energy.

The simulated spectrum

1 week after irradiation

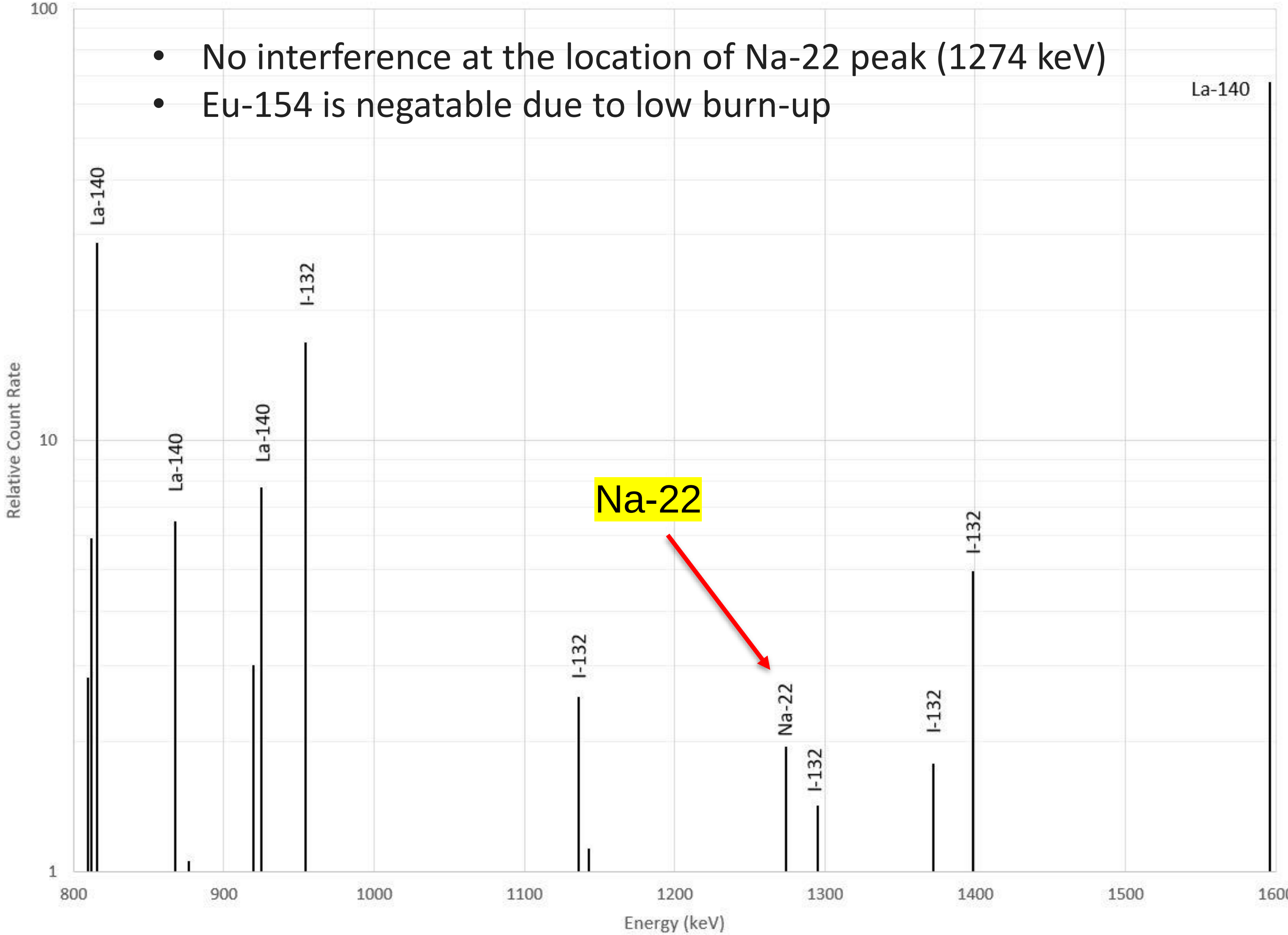


Caveats:

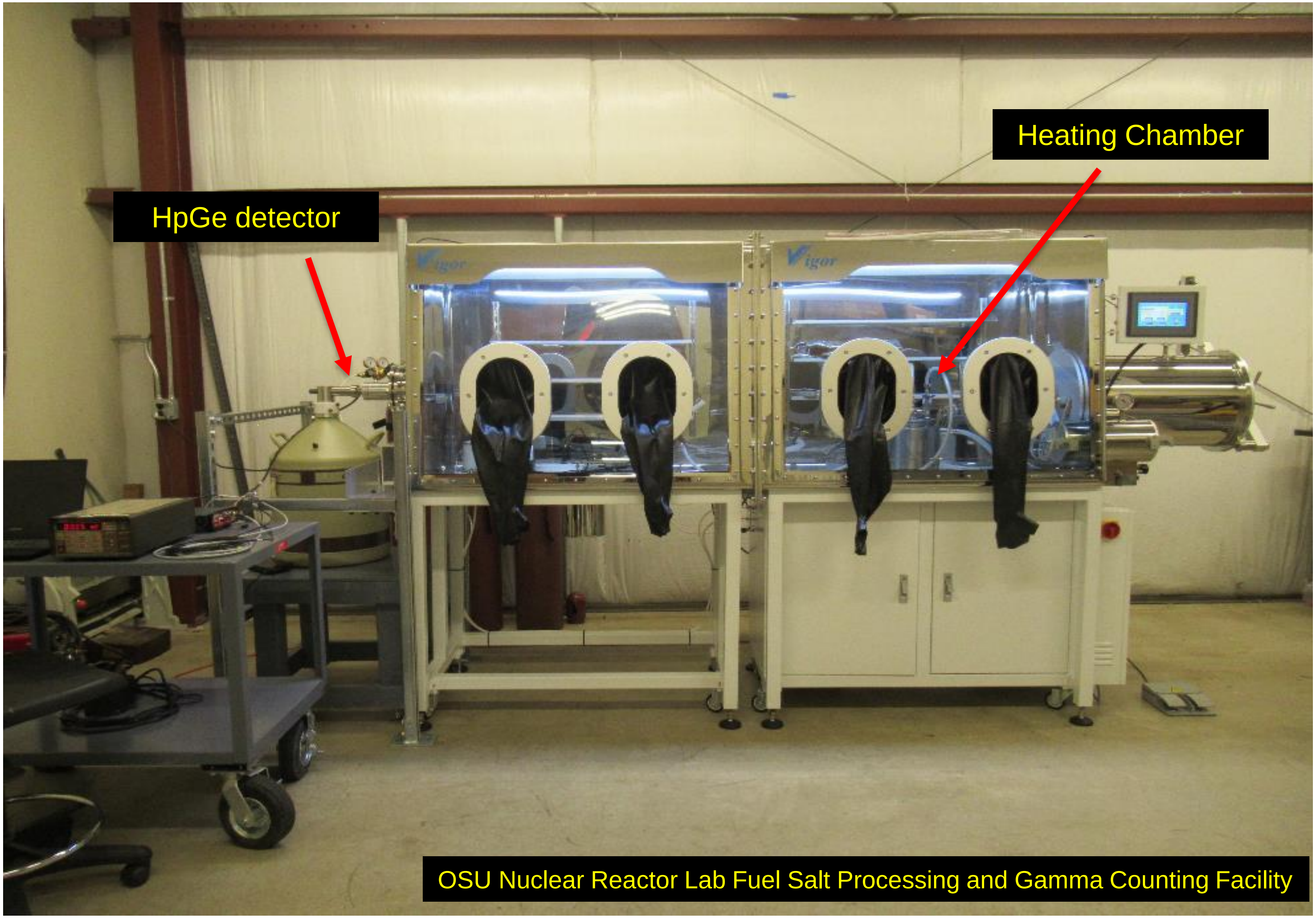
- Relative count rate, not absolute.
- No Compton continuum.
- A hundred other nuclides with lower activities aren't included

The simulated spectrum

- No interference at the location of Na-22 peak (1274 keV)
- Eu-154 is negatable due to low burn-up



Newly build OSU fuel salt processing facility at Nuclear Reactor Laboratory



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Step 1: Adding Na-22 tracer ($^{22}NaCl$)

- A sample of 100 µL of liquid source, $^{22}NaCl$, was transferred by pipette to the empty vial.
- The vial was heated in an oven at 60°C for one hour.
- The temperature was then increased to 80°C and the vial was heated for another 30 minutes to complete the evaporation.
- After allowing the vial to cool, it was covered and transferred to the HpGe, a spectrum was collected with the vial on the platform used for the calibration.
- A quartz disc (thickness 1.5 and 3 mm) was positioned on a platform approximately 38 cm above the detector endcap to calibrate self-attenuation of the quartz bottle. A traceable point source of Na-22 was then placed on the quartz disc.

Table. Na-22 assay

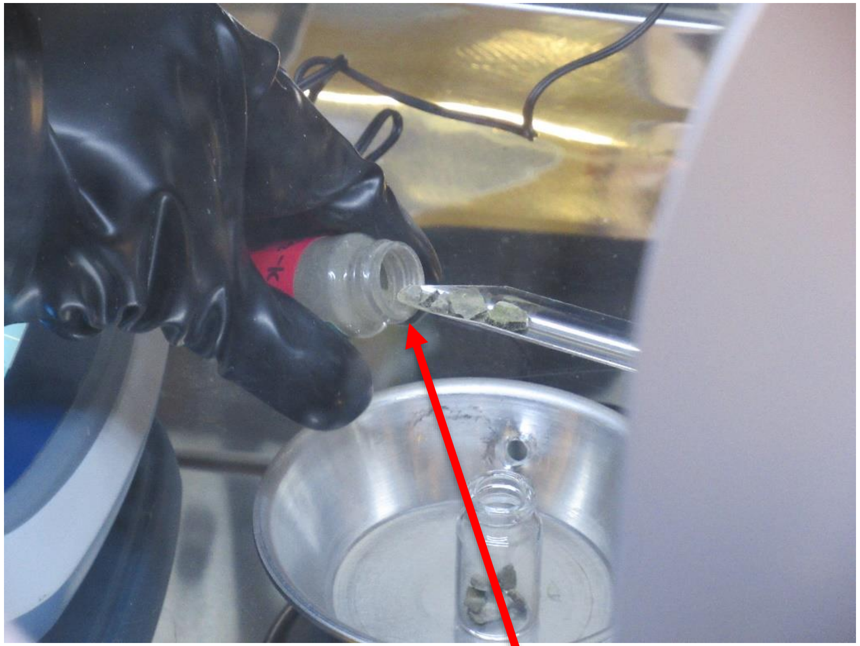
		Uncert (%)
Count Date:	03/10/23	
Live Time (s):	2000.8	
Peak Counts:	11330	0.94
Rate (cps):	5.663	0.94
Peak Eff (pcm):	9.01	1.35
Em Rate (kgps):	62.8	1.64
Activity (µCi):	1.70	1.64

Sealed double capsuled salt sample

HpGe detector

Step 2: Adding fuel salt for in-core irradiation

Quartz Bottle Mass	**10.99 g**
Added $^{22}NaCl$	**0.1 mL (1.7 µCi)**
Fuel salt mass	**6.065 g**
U-235 in sample	**1.21 mg**

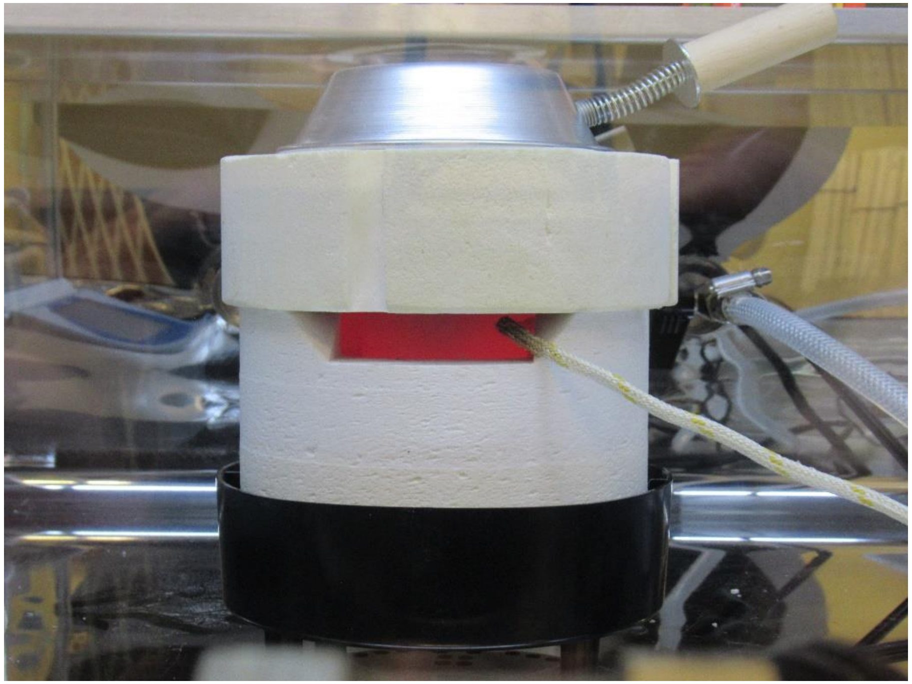


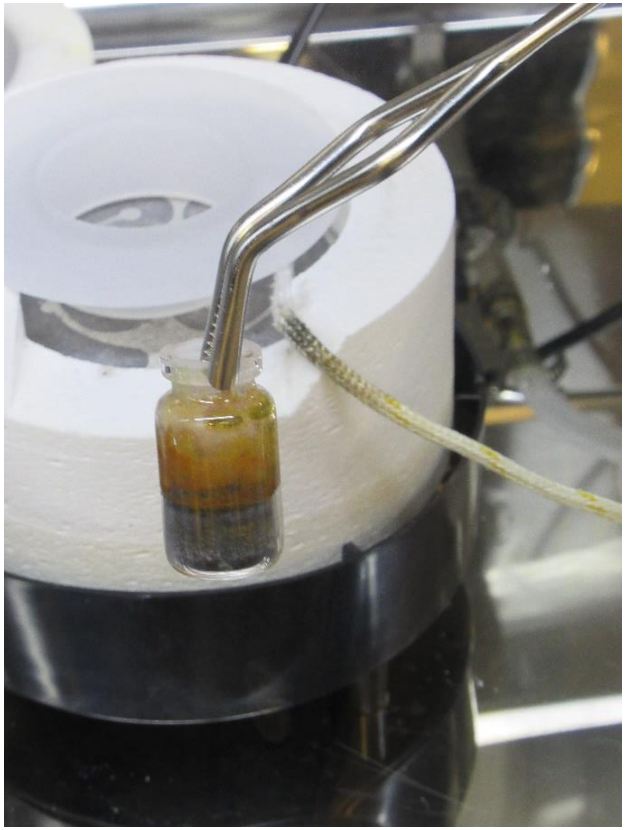
Fuel salt is being added into quartz bottle for irradiation

$MgCl_2$-KCl-UCl_3 (DU) composition:

- U-235 concn in salt sample at 0.02 wt%
- U-238 concn in salt sample at 12.14 wt%.
- **U-235 enrichment 0.2%**

Step 3: Melting fuel salt to mix with $^{22}NaCl$



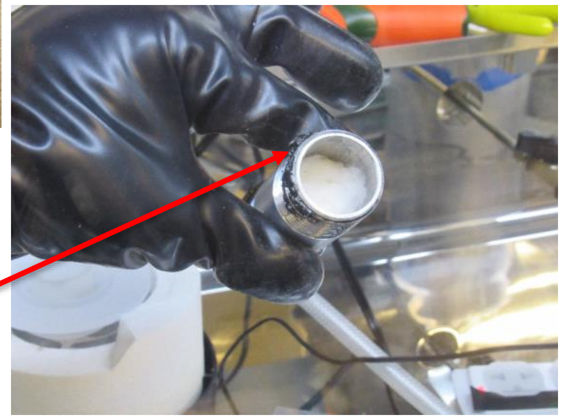


Heating Scheme in Ar glovebox:

- Temp raised to ~ 500°C for 30 min
- Verified in molten state
- Continued heating 500−550°C for 2 hours (to allow mixing of $^{22}NaCl$ with fuel salt)

- Once cooled, the bottle was weighed and crimp sealed with Grafoil/aluminum cap.

Step 3: Preparing encapsulation of fuel salt and ^{22}Na for in-core irradiation



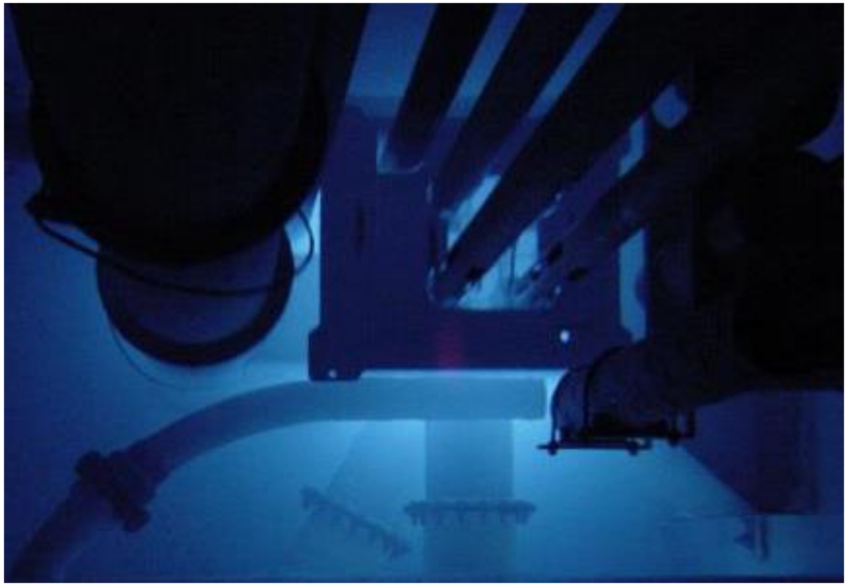
Grafoil paste for sealing Aluminum cap

- Silica insulation inserted as cushion above quartz bottle.
- Initial spectroscopy conducted at heights of 38 cm and 67 cm above the HPGe detector end cap.
- Measurements were repeated with a 0.1 inch thick lead sheet underneath, which will be used for reducing dead time at post-irradiation.

Step 4: In-core irradiation

Fission product gasses produced from 15 grams of salt mixture (ORIGEN)

Nuclide	Activity (Ci)	Activity (Bq)	Half-Life (days)	l (1/s)	# atoms	Moles (mol)
I-131	3.91E-05	1.45E+06	8.025	1.00E-06	1.45E+12	2.40E-12
I-132	1.44E-04	5.34E+06	0.096	8.39E-05	6.36E+10	1.06E-13
I-133	1.88E-03	6.97E+07	0.868	9.24E-06	7.54E+12	1.25E-11
I-134	3.71E-02	1.37E+09	0.036	2.20E-04	6.25E+12	1.04E-11
I-135	1.17E-02	4.32E+08	0.149	5.38E-05	8.03E+12	1.33E-11
Kr-85m	3.16E-03	1.17E+08	0.187	4.30E-05	2.72E+12	4.53E-12
Kr-87	1.93E-02	7.16E+08	0.053	1.51E-04	4.73E+12	7.85E-12
Kr-88	1.40E-02	5.18E+08	0.118	6.82E-05	7.60E+12	1.26E-11
Xe-131m	3.24E-10	1.20E+01	11.840	6.78E-07	1.77E+07	2.94E-17
Xe-133	3.97E-06	1.47E+05	5.248	1.53E-06	9.60E+10	1.59E-13
Xe-133m	7.38E-07	2.73E+04	2.198	3.65E-06	7.49E+09	1.24E-14
Xe-135	6.23E-04	2.31E+07	0.381	2.11E-05	1.09E+12	1.82E-12
Xe-135m	3.72E-03	1.38E+08	0.011	7.56E-04	1.82E+11	3.03E-13
					Total =	6.61E-11



Picture of in-core irradiation at OSURR

Thermal Neutron Flux: 6.0×10^{12} n/cm^2/s

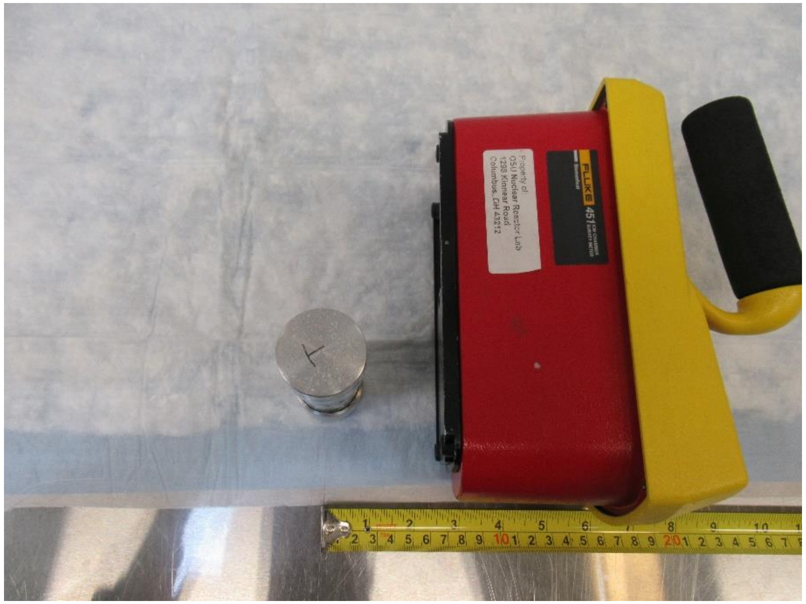
Total Neutron Flux: 1.1×10^{13} n/cm^2/s

Irradiation time: 1 hour

Fluence: 3.96×10^{16} n/cm^2

Step 5: Post-irradiation results

Dose rates after 10 days



10 cm from centerline:

Gamma	13.3 mrem/h
Gamma + Beta	15.4 mrem/h

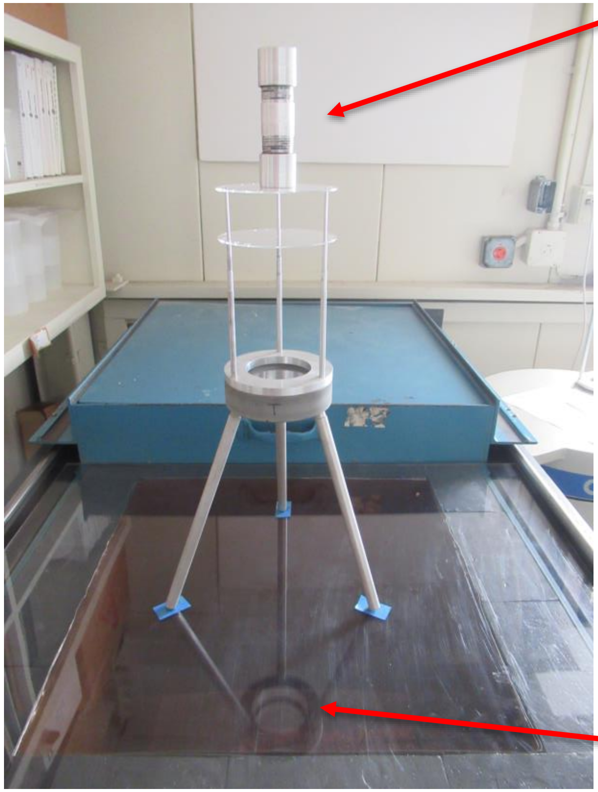
30 cm from centerline:

Gamma	1.76 mrem/h
Gamma + Beta	1.96 mrem/h

* On contact gamma + beta ~ 31 mrem/hr

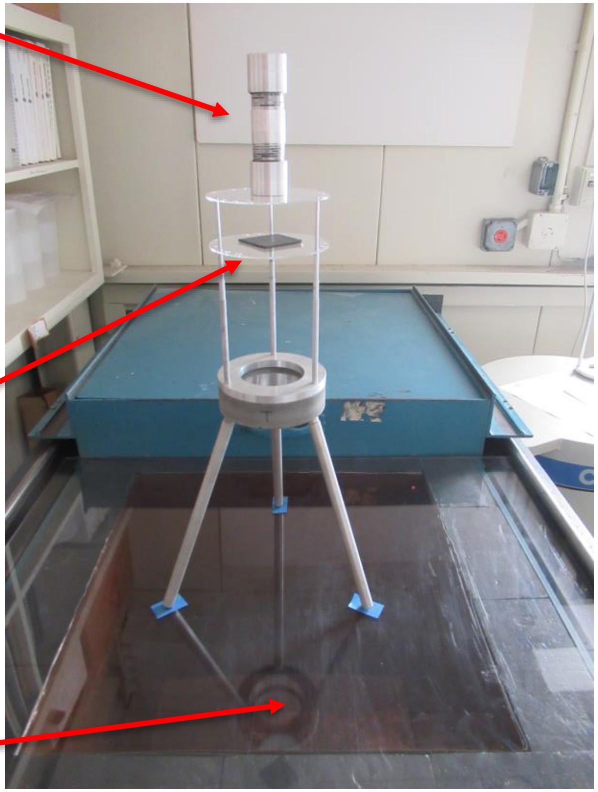
Step 6: Post-irradiation results (10 days)

Irradiated fuel salt inside double encapsulation



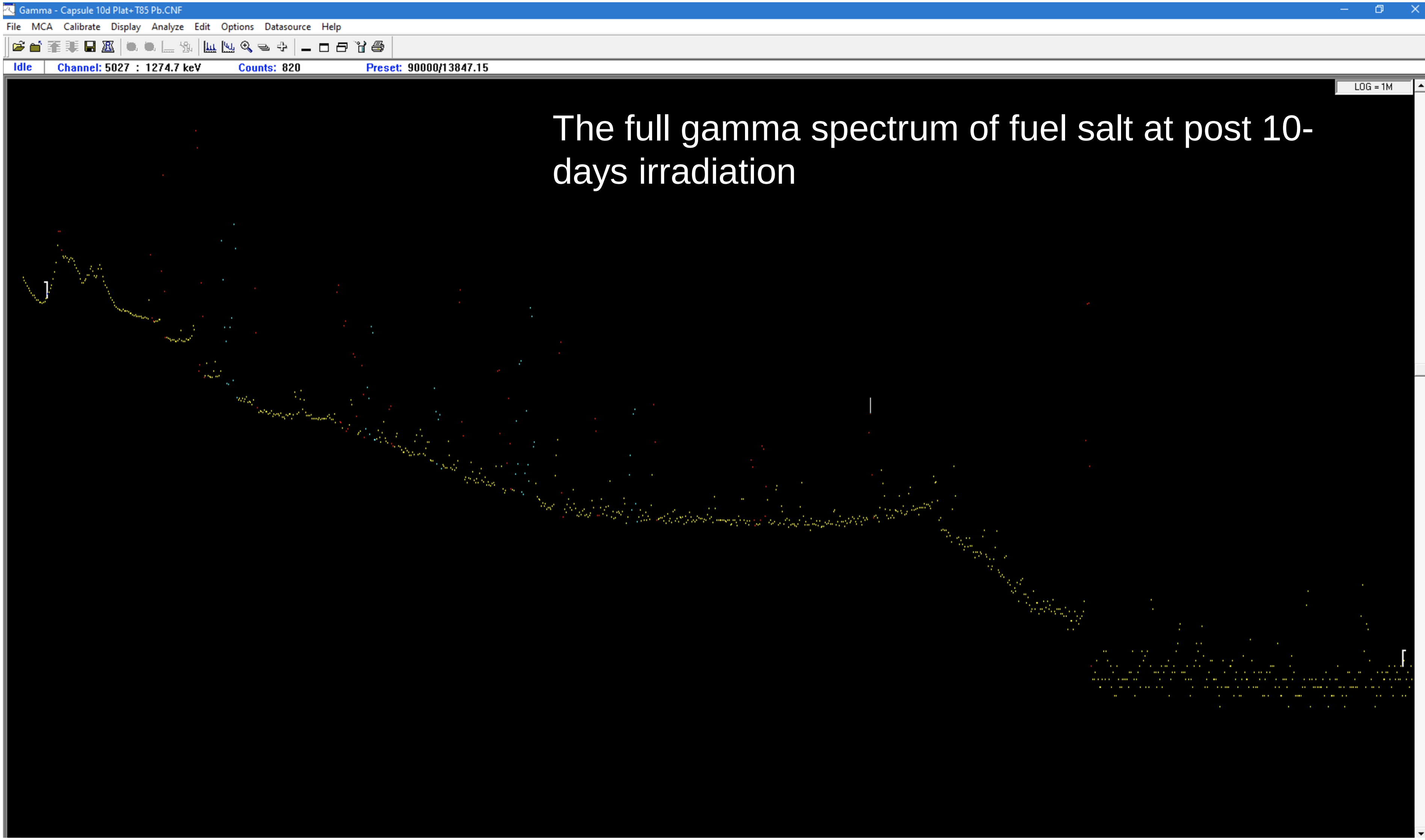
Pd sheet

HpGe Detector



Open Air (67.63 cm from detector)
Dead Time: 3.38%

Pb (2” x 2” x 0.1” inch) shielded
Dead Time: 0.66%


Gamma - Capsule 10d Plat+T85 Pb.CNF
File MCA Calibrate Display Analyze Edit Options Datasource Help
Idle Channel: 5027 : 1274.7 keV Counts: 820 Preset: 90000/13847.15
LOG = 1M
The full gamma spectrum of fuel salt at post 10-days irradiation

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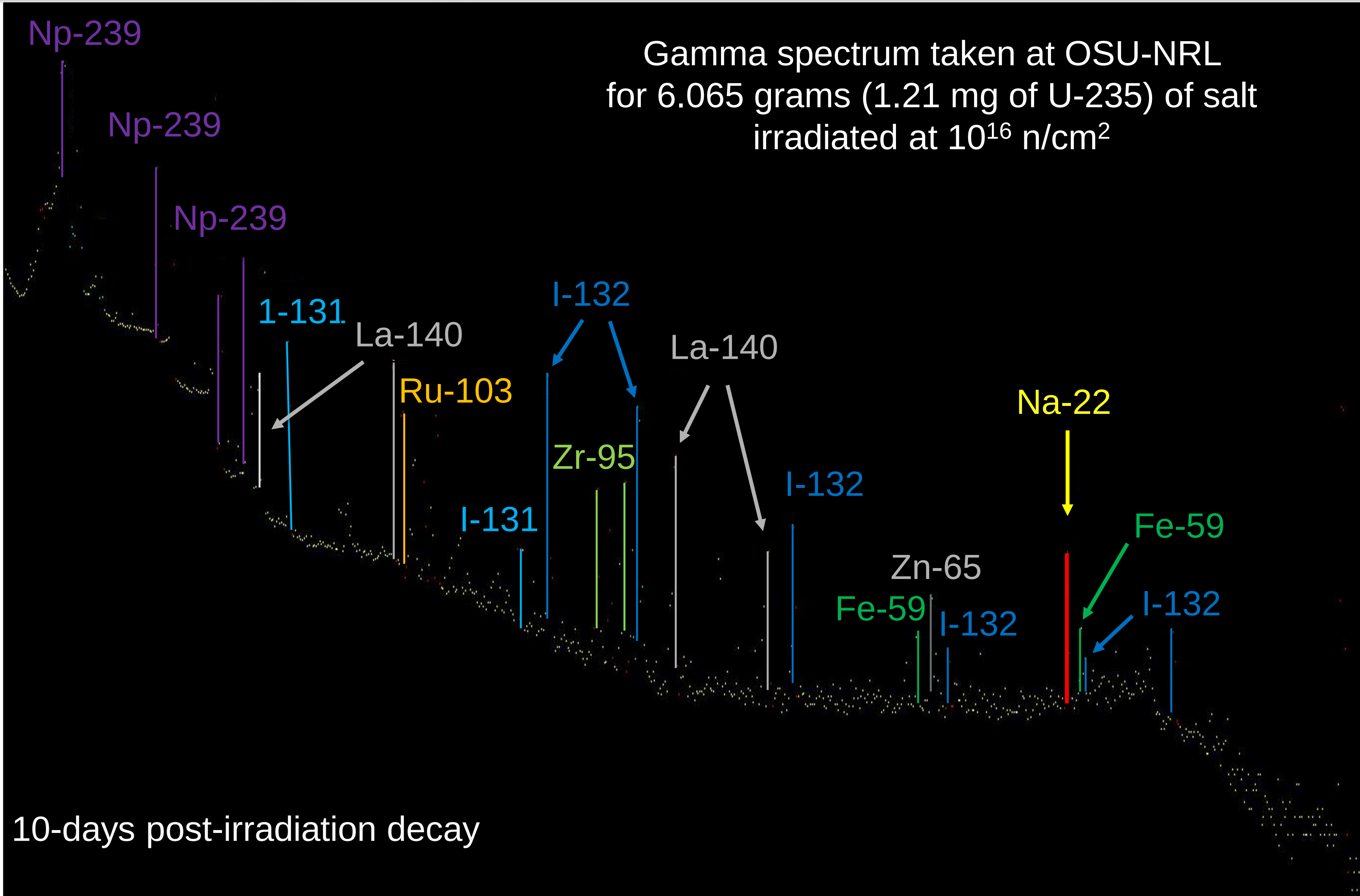
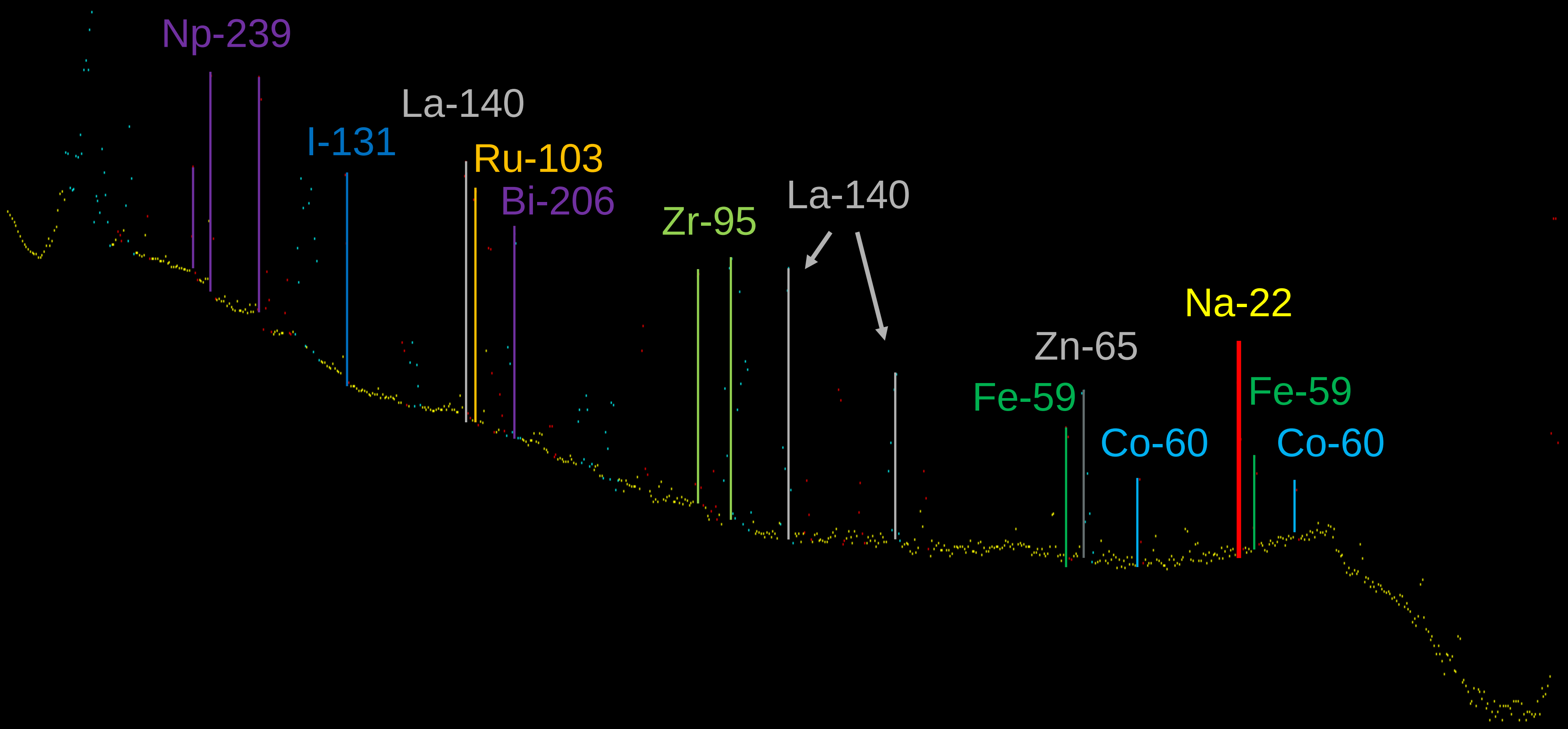


Gamma spectrum taken at OSU-NRL
for 6.065 grams (1.21 mg of U-235) of salt
irradiated at 10^{16} n/cm^2



21-days post-irradiation decay

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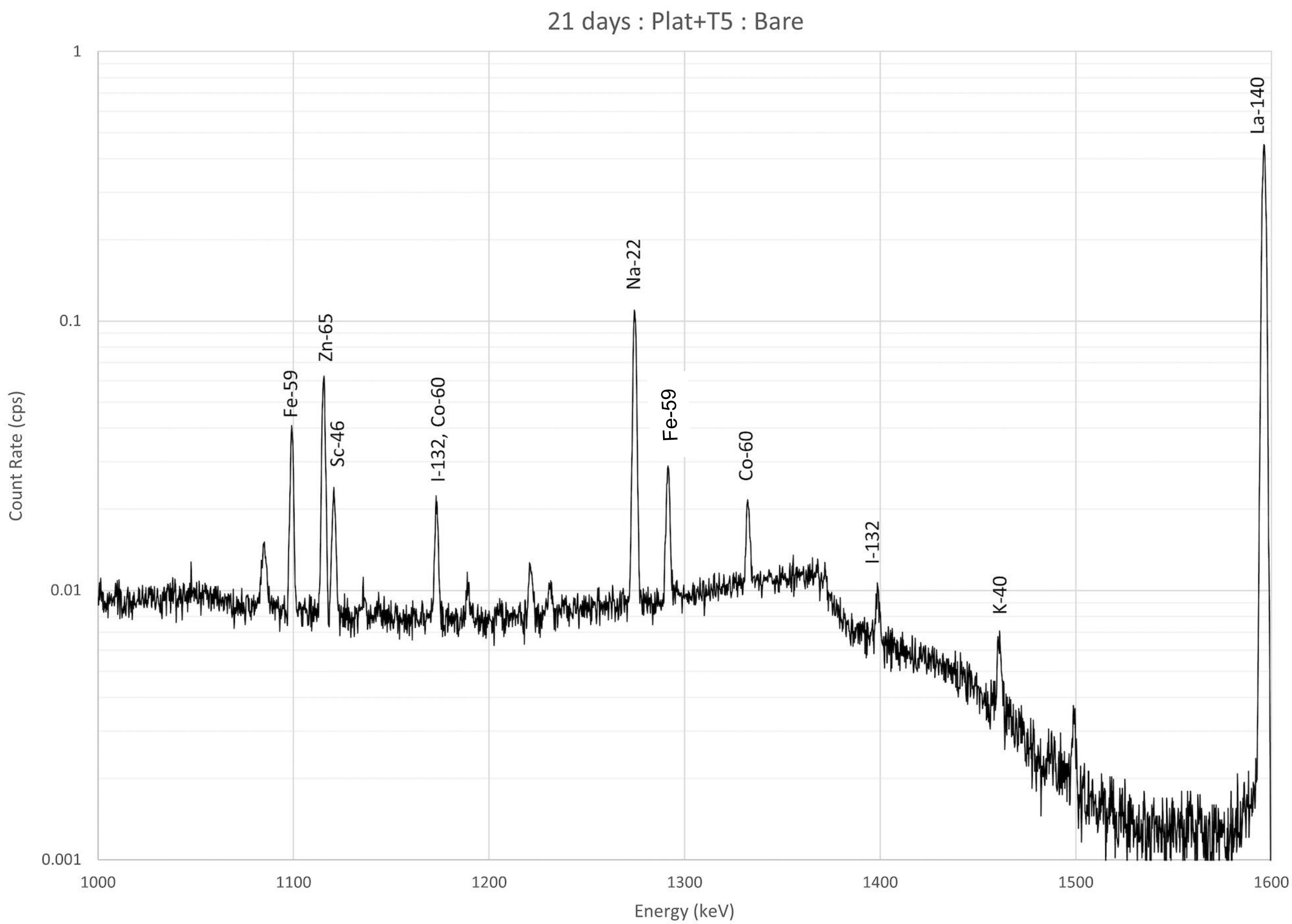
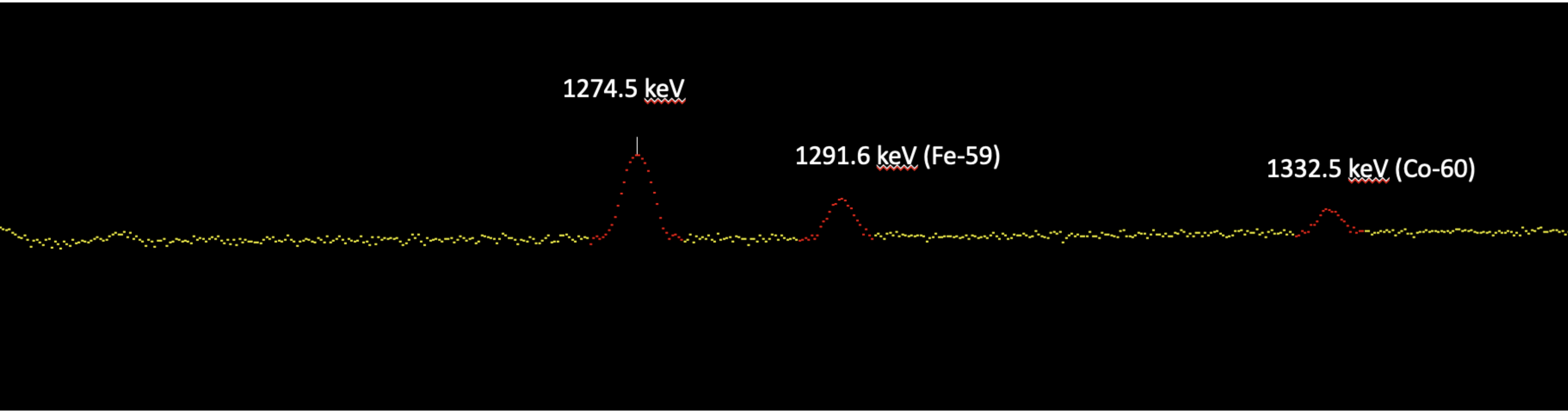
Zoom-in region of fuel salt at post 21-days irradiation



Zoom-in Na-22 peak region of fuel salt at post 10-days irradiation

- Na-22 (1274.5 keV) neighborhood is cleared off any sign of interferences with current burn-up
- Fe-59 comes from impurity in salt



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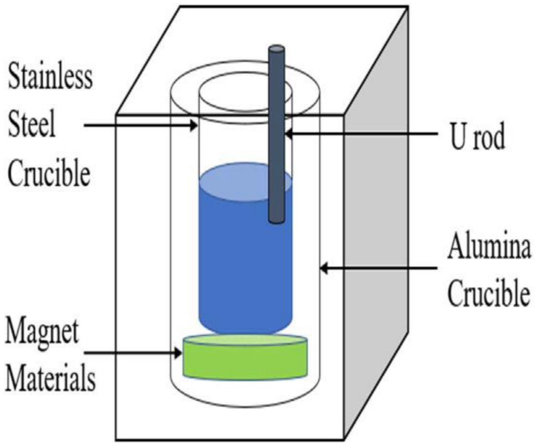

Schematic for preparing UCl_3 salt from DU metal rod and NaCl-KCl-$FeCl_2$

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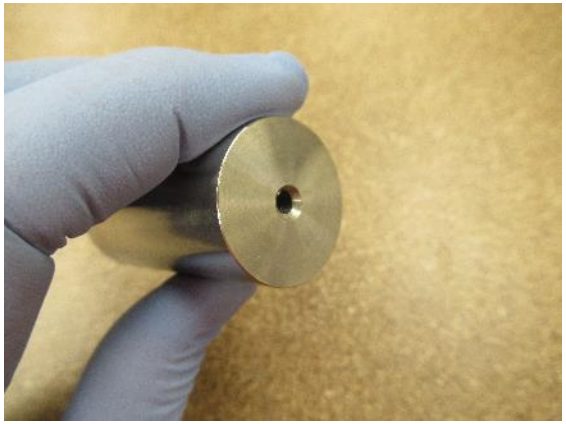
Heating Chamber and off-gasing

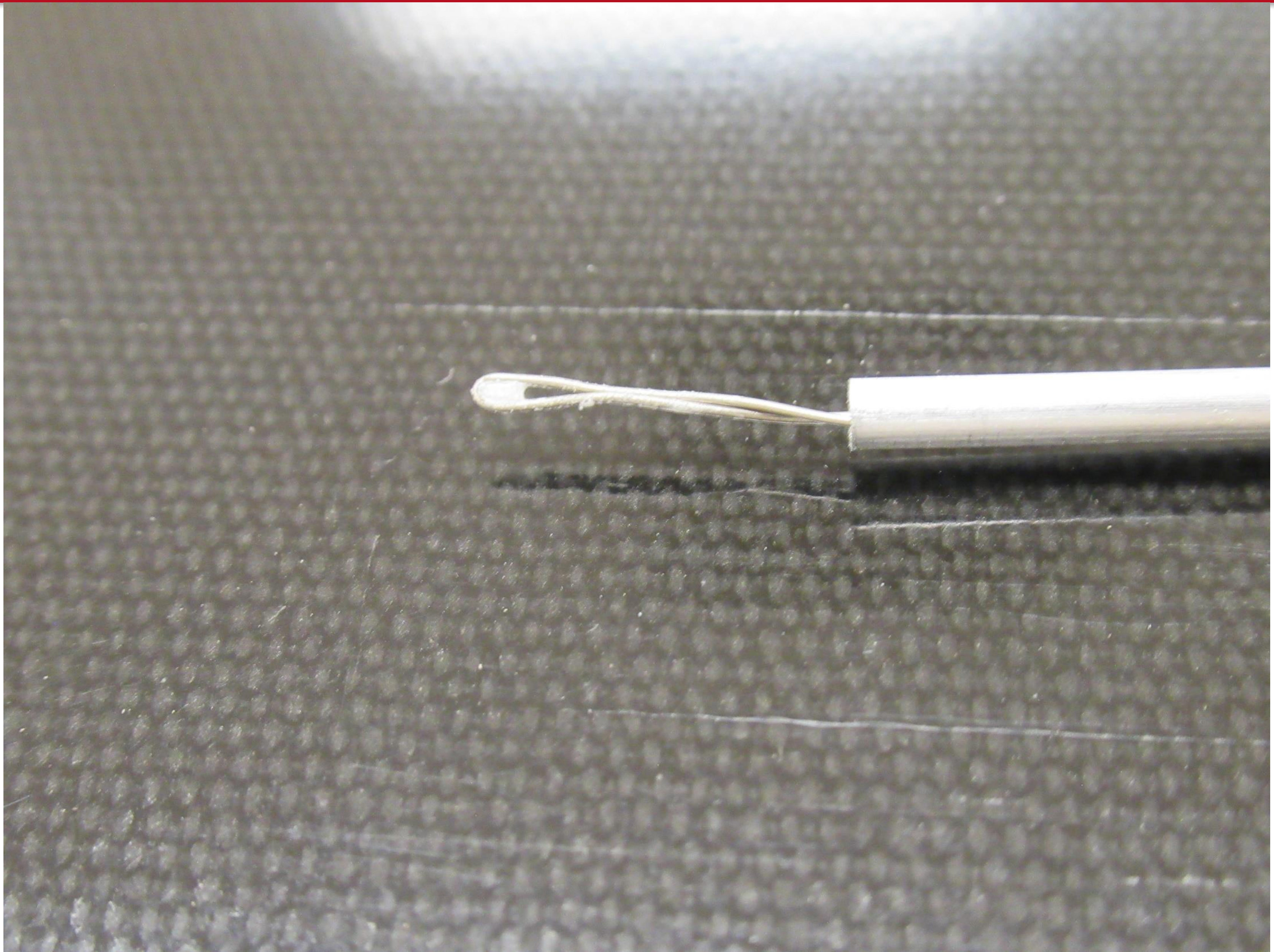
Salt extraction apparatus



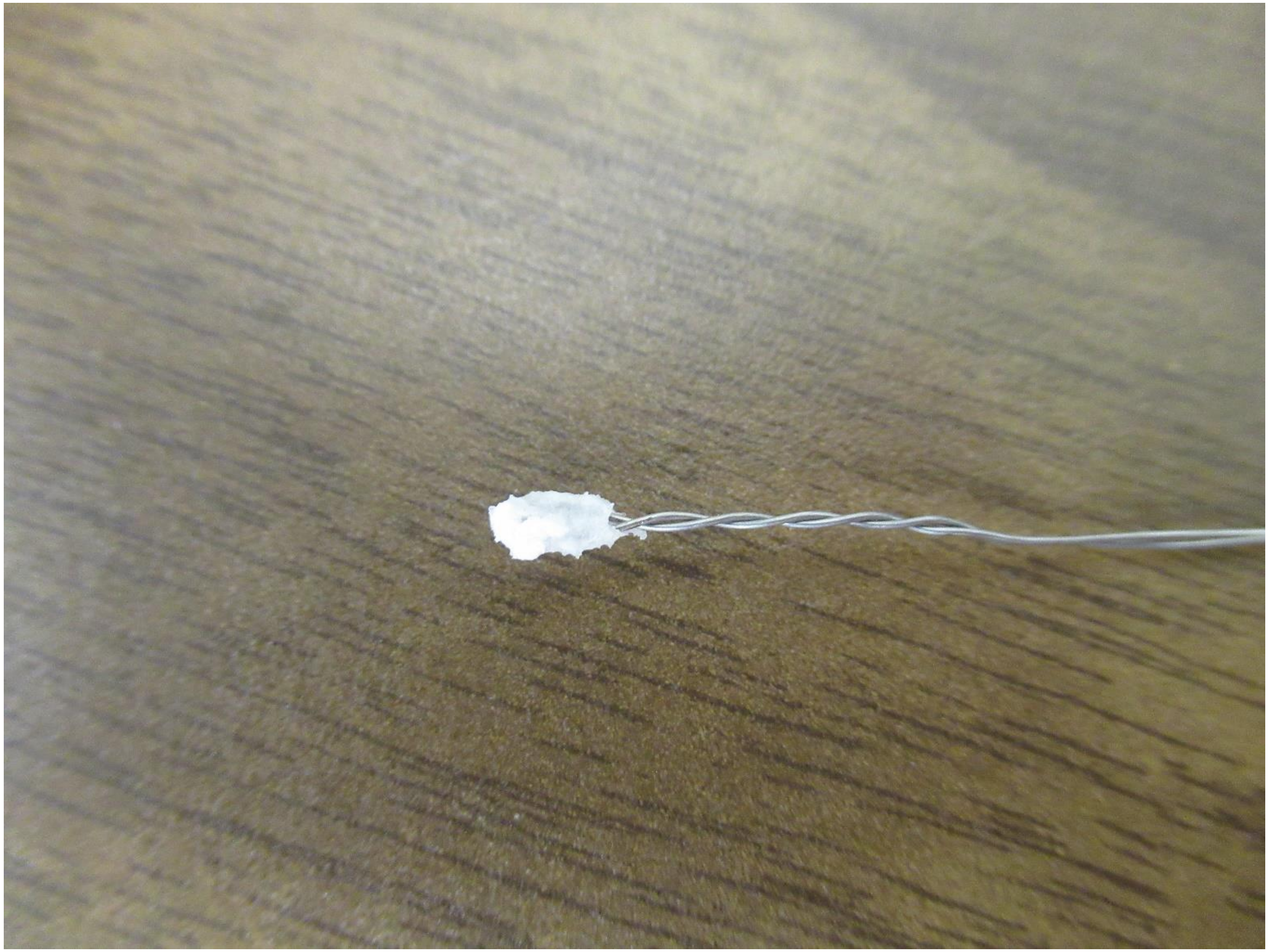



Photos showing venting and alignment apparatus for sampling within central tube

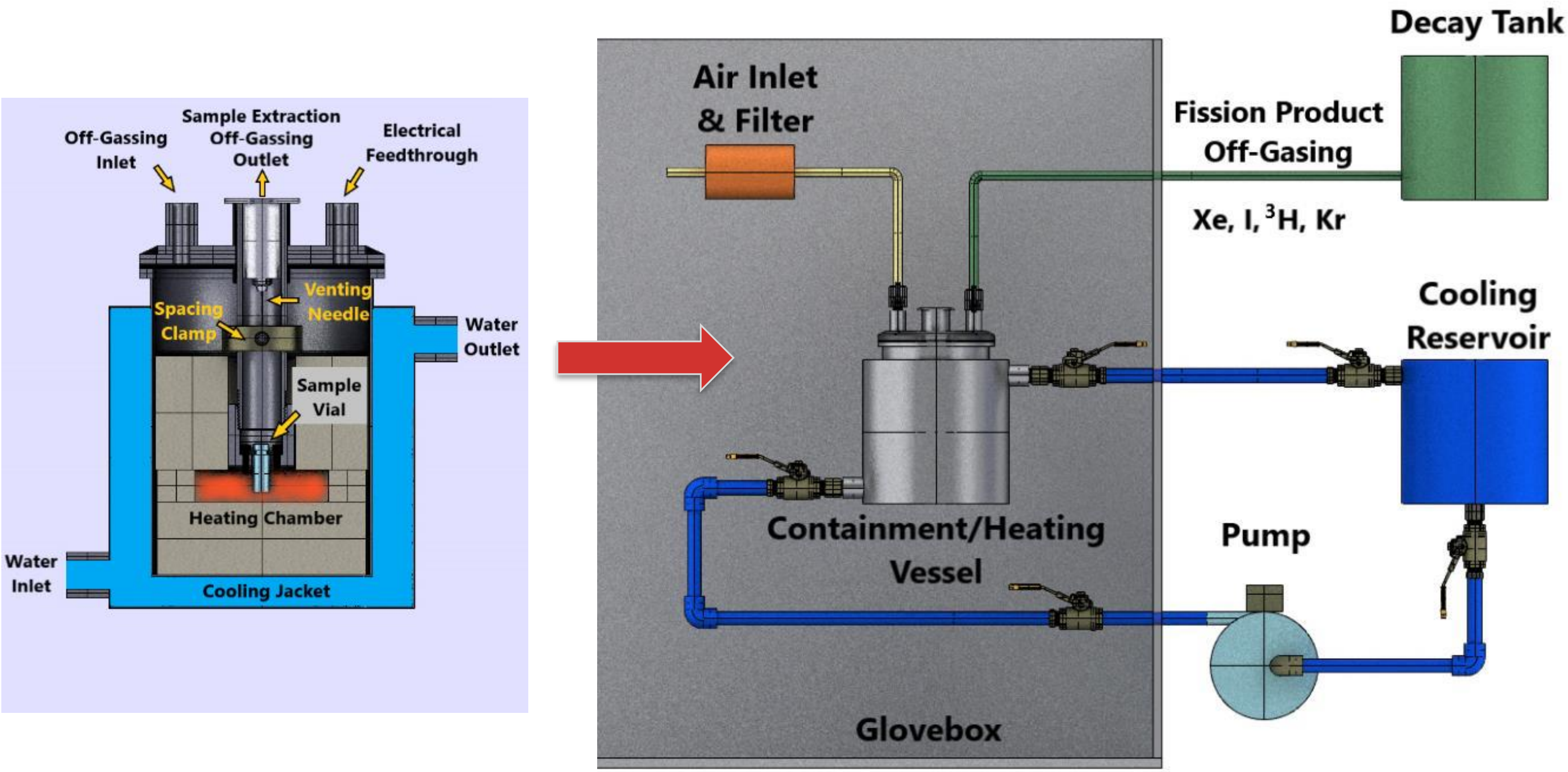
Fuel salt sample extraction practice



Fuel salt sample extraction practice



Our facility is capable of off-gassing study



Summary

- 6 gram of salt (1.21 mg of U-235) was successfully irradiated at OSU Nuclear Reactor (3.96×10^{16} n/cm^2), gamma spectra of fission products with added Na-22 tracer was acquired
- No other interferences peak identified. Good News! Eu-154 interferences was well understood, and it does not present an issue due to low burn-up
- A thin piece of lead between the source and detector is effective in reducing deadtime, 121 keV Eu-154 is blocked, but higher energy of Eu-154 at 723 keV is still unobscured for spectrum correction
- This could be a real-time method, depending on burn-up, deadtime from short-lived fission products, sampling mass, etc.
- Demonstrated the fuel salt irradiation experiment (first since MSRE?)

Near-term and long-term plan

- Next step (by 12/31/2023) is to increase burn-up and test irradiated fuel salt sample extraction
  - DU to natural U
  - 1 hour to 7 hours irradiation
  - Reduce Na-22 from 1.7 µCi to ~ 100 nCi
- Future study is to find out Na-22 burn-up and large volume molten salt testing for an extended burn-up (proposing new project)
  - Na-22 neutron capture x-section is 29,260 barn @ 25 meV
  - It will be burned away after x days of spiking – self elimination!
  - Reached out to Abilene Christian university
  - Simulate and even measure in a large-scale fuel salt system

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Praneeth Kandlakunta

Nuclear Reactor Lab

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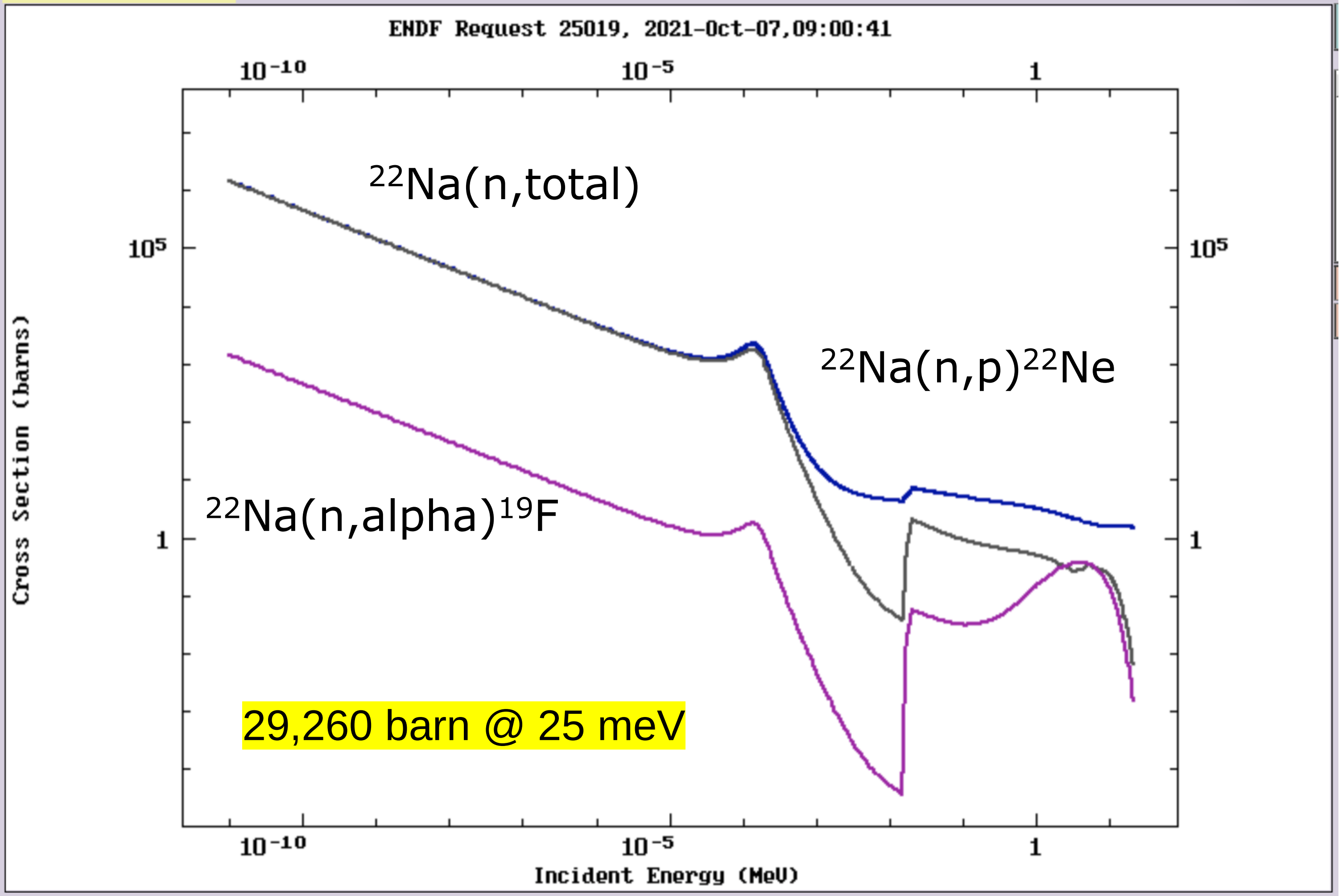
Thank you for your attention!

Challenges with tracer burn-up

- Na-22 has a significant neutron absorption cross-section



https://www.nndc.bnl.gov/

Radioisotope Selection

Two or more gamma lines in one isotope might be used to verify each other or in case one has an interference

May add two isotopes to validate each other or in case one has an interference

Na-22 is the best option

	Na-22	Co-60	Na-24	Br-82
Decay mode	β+	β-	β-	β-
Main gamma energy/keV	1274.54	1173.23; 1332.50	1368.63; 2754.01	554.35; 619; 776.52;1044
Half life	2.6018 y	1925 d	14.977 h	35.28 h
Comments	Not a fission product	Selective bounding?	$T_{1/2}$ too short	$T_{1/2}$ too short

Challenges: Off-gas Constituents

Table 1

Potential species in the cover gas of an MSR.

Type of cover gas constituent	Example species
Mists, aerosols, and particles	Salt residues, graphite debris for graphite-moderated fluoride systems, corrosion products, and noble metals (e.g., Ru, Pd, Rh)
Gases and volatile species	^3HF, HF, F_2, Cl_2, Br_2, I_2, Ar, interhalogens (e.g., ICl, IF_5, IF_7), volatile halides, and the decay products (e.g., Cs, Ba, Rb, Sr, La, Br, I, Se, Te) (Ostvald et al., 2009)
Tritium	$^3H_{2(g)}$, $^3HH_{(g)}$, $^3HF_{(g)}$, $^3HF_{(l)}$, and possibly $^3HHO_{(g)}$ and/or $^3H_2O_{(g)}$
Short-lived fission gases and their daughters	^{139}Xe $t_{1/2} = 39.5$ s, ^{137}Xe $t_{1/2} = 3.83$ min, ^{135m}Xe $t_{1/2} = 15.3$ min, ^{135}Xe $t_{1/2} = 9.1$ h, ^{133m}Xe $t_{1/2} = 2.19$ d, ^{133}Xe $t_{1/2} = 5.25$ d, ^{90}Kr $t_{1/2} = 32.3$ s, ^{89}Kr $t_{1/2} = 3.18$ min, ^{88}Kr $t_{1/2} = 2.84$ h
Longer-lived radionuclides	^{129}I $t_{1/2} = 1.57 \times 10^7$ y, ^{79}Se $t_{1/2} = 6.5 \times 10^4$ y, ^{85}Kr $t_{1/2} = 10.7$ y, ^{36}Cl $t_{1/2} = 3 \times 10^5$ y

Source: *Andrews, Hunter et al. "Review of molten salt reactor off-gas management considerations." Nuclear Engineering and Design **385** (2021): 111529.*